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Quantitative Assessment of the Condensed Phase Heats of Reaction in a Double Base Propellant

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Abstract. Heat of decomposition of the double base propellant has been calculated from the knowledge of the composition and decomposition enthalpy of the ingredients. This was compared with the experimentally observed value of the propellant decomposition which suggested that condensed phase contribution is very marginal (one twentieth of the total calorimetric value) in double base propellants unlike composite solid propellants where condensed phase contribution is as high as one third. The condensed-phase in double base propellant was attributed to the nitration of the 2*n*-diphenylamine stabilizer in the propellant matrix.

1. Introduction

It has been shown conclusively from kinetic and thermodynamic approach that condensed phase reactions play a significant role during the composite propellant combustion and that the condensed phase reactions contribution is one third of the total combustion at ambient pressure[1]. In literature qualitative and quantitative contribution of phase reactions is not reported for Double Base Propellants (DBP). It was therefore thought, to examine this aspect from the view point of occurrence of condensed phase reactions in DBP.

2. Experimental

The composition of the DBP used in the present investigation is given in Table 1 and reference 2. Thermochemical approach was adopted in collecting the data of heats

of decomposition and combustion of DBP. For such studies, experiments were carried out by using Differential Scanning Calorimeter (DSC), Thermogravimetry (TG) and Adiabatic Bomb Calorimeter. In the present work Perkin-Elmer DSC-2 B and TGS were used and operations were carried out according to the manufacturer's instructions. In DSC and Dynamic TG experiments the quantity of the sample taken, in aluminium cups, was 1.5 to 3.0 mg. The runs were carried out in ultra high pure nitrogen gas flowing in the system at a rate of 30 ml/min. The thermograms of DBP and its ingredients are shown in Fig. 1 and the results are shown in Table 1. Conventional adiabatic bomb calorimeter was used in the present work and for the temperature measurement Hewlett Packard Quartz thermometer model 2801A was employed. The results for DBP is given in Table 2.

3 Results and Discussion

DNT, TNT, NG and 2-nDPA showed endothermic transformations/decompositions through out the range (25-320°C). For NG the earlier reported information was only

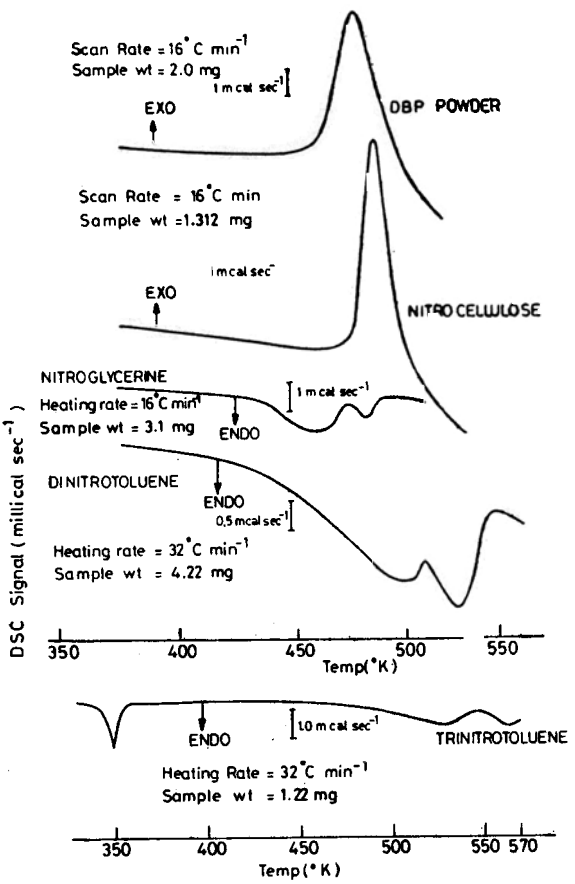

Figure 1, DSC thermograms of double base propellants and its ingradients.

Table 1 Thermo-chemical data of DBP propellant and its ingredients.

Compound	DBP Propellant Wt (%)	*MP* (°C)	*BP* (°C)	Decomposition temp. (°C)	Heat of decomposition (cal/gm)
NC	57.5		197 (decomposed)		—336
NG	26.5	145	145	205 (endo)	+47.3
DNT	3.0	65	227	252 (endo)	+118.8
TNT	3.0	76	252	285 (endo)	+165
2-*n*DPA	1.5	74	277		
Other ingredients	8.5	—			
Propellant powder	—	—		209 (decomp)	−210

one endotherm which was attributed to the voltalisation of NG (140-180°C) by Ayres and Ben[3], as evidenced from their DTA thermograms at heating rates 4-6°C/min. The results showed a peak at 189°C although the pen excursion began at 145°C. The present investigation was carried out with the DSC instrument wherein the sample was sealed in an aluminium cup. NG was scanned at the rate of 16°C/min with a sensitivity of 16 m.cal/sec. The thermogram, thus recorded, indicate that there are two endothermic steps in thermal decomposition of NG. The peak at the temperature (145°-187°C) is observed to be due to vaporization. The second endothermic peak is observed at 204°C which has not been reported earlier. The second peak (endothermic) is attributed due to the thermal decomposition of NG via $O\text{-}NO_2$ bond breakage. It is envisaged that the NG first vaporises and then decomposes endothermically. It may be pointed out here that partial decomposition of NG in addition to vaporization has been observed by Ayres & Bens[3] in the differential thermal analysis of NG.

Deason[4] reported the exothermic decomposition of Dinitrotoluene (DNT) at 162°C. Krein's[5] reports on DNT, by using DTA, indicated the melting point at 70.5°C and ignition at 358°C. However, present results from DSC experiments show no exotherm, instead two endotherms were noticed, one at 217°C and the other at 252°C, besides a peak due to the melting at 65°C. These runs were carried out at a scan speed of 32°C/min. It is reasonable to attribute the peak at 220°C (DSC) to the vaporization of DNT and the second peak to endothermic decomposition. Neither Deason[4] nor Krien[5] reported this observation.

Regarding Trinitrotoluene (TNT) Krien[5] said that there was an endothermic decomposition at 250°C, from DTA results. In the present investigation, once again, two endotherms were noticed one at 252°C and the second at 285°C at the heating rate of 16°C/min. The peak observed in DSC thermogram at 252°C, is due to the vaporization of TNT and peak at 285°C may be due to the endothermic decompositon of TNT.

NC decomposes exothermically at 193°C when it is heated at the rate of 10°C/min. The DSC thermogram of NC indicates only one peak due to the exothermic decomposition.

It is seen from Table 1 that all the compounds except *NC* melt/vaporise first. The melting/vaporization are seen to be endothermic. The thermal decomposition of *NC* and DBP showed only one peak (exothermic decomposition). The experimental value for the total heat of vaporization/decomposition for all the ingredients were calculated by measuring the areas under the curve which were converted into caloric output. The values are shown in Table 1. It is seen from the Table 1 that the experimental value for the heat of thermal decomposition of DBP is 210 cal/gm. The heat of decomposition (ΔH) of DBP was calculated from the knowledge of heat of the decomposition of the individual components. The following equation was used :

$$\Delta H = \Sigma H_i X_i$$

where H_i and X_i represent the heat of the decomposition and the fraction of the ith component respectively present in the DBP. The ΔH value calculated in this way comes out to be 168 cal/gm which is much lower (by 42 cal/gm) than the experimentally observed heat of decomposition (210 cal gm^{-1}) of the propellant by DSC. This would mean that the heats of decomposition are not additive and that there occurs an exothermic condensed phase reaction in DBP. Similar observation in the case of composite propellants have been reported earlier[1]. In the case of DBP the condensed phase reactions contribution, as shown above, is only 42 cal/gm whereas for polystyrene (PS)/ammonium perchlorate (AP) composite propellants it was much higher[1]. From mass spectrometric analysis of the thermal decomposition gases of PS/AP it was found that[1,8] the mas spectra of the ingredients of composite propellant differed from those of the decomposition gases of the propellant itself. The behaviour was explained on the basis of the interaction of AP and PS decomposition products in the porous matrix of the propellant.

To have an insight into the mechanism of the heterogeneous condensed phase reactions in DBP, partially decomposed propellant was analysed to gather knowledge about the intermediate products. The propellant decomposition residue were collected. The partially decomposed residue was dissolved in dichloromethane. The solution was filtered off. The residue would contain NC and some inorganic salts. The aliguot was concentrated and then subjected to TLC analysis. The eluant system was benzene/petroleum ether/ethyl acetate (12:12:1). The chromatographic plate was removed and dried in air. The saturated solution potassium hydroxide was sprayed on the plate. The chromatogram showed the presence of TNT and four other bands. These were identified as nitroderivates of 2-*n*DPA. This suggests that during thermal decomposition, nitration of 2-*n*DPA takes place. Since the nitration of 2-*n*DPA is an exothermic process, the excess of heat liberated during the thermal decomposition of 2—*n*DPA must be coming out as a result of this nitration. The calorimetric values obtained in the present work and that of literature are shown in Table 2. The estimated

Table 2. Calorimetric values of DBP and the ingredients.

Compound	Heat of explosion or heat liberated (N_2 atmosphere) (cal/gm)	Reference
NC	833	Present work
	855	AMCP[10]
	973	Fedroff, B.T[11]
NG	1485	Fedroff, B.T[11]
	1600	AMCP[10]
	1470	Escales[12]
DNT	860	AMCP[10]
TNT	882	AMCP[10]
2-*n*DPA	14.88	AMCP[10]
DBP	880	Clayton[13]
	885	Present work

alue for the total combustion is around 825 cal/gm whereas the total heat of decompositionf or DBP is only 210 cal/gm out of which the condensed-phase heat release is only 42 cal/gm. When the total heat of combustion of DBP is compared with the heat of condensed phase reactions, it is around 1/20 th. It may be interesting to mention here that similar estimations in composite propellant have yielded the condensed phase contributions[9] as high as one third. The data of composite propellants together with double base propellants is presented in Table 3.

Table 3. Condensed phase enthalpy for composite and double base propellant.

Component	Enthalpy (cal/gm)
Composite propellant	492
Ingredients of composite propellant	209
Estimated condensed phase heat release in composite propellant	283
Double base propellant	210
Ingredients of double base peopellant	168
Estimated condensed phase heat release in double base propellant	42

If one compares with the values of condensed phase reactions, heat release for composite propellant and DBP which are 283 cal/gm and 42 cal/gm respectively, it looks reasonable to say that the condensed phase heat release is much less in DBP. This suggests that in DBP the condensed phase heat release is coming from only nitration of the stabiliser which is present in small proportions in the composition. On the other hand in composite propellants there is a significant interplay between oxidizer and fuel for the condensed phase heat release[1]. In the case of DBP most of the components are volatile and hence the interplay between the oxidising and fuel species in the condensed phase is very significantly lower.

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